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APPLICATION OF PATENT OF INVENTION

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(54) **Epoxy-elastomer composite material and manufacturing process of said material.**

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The present invention relates to composite materials made up with elastomer and adhesive of the type currently named "epoxy resin", although it is rather an intermediate for making a resin, and the invention subject is more particularly an epoxy-elastomer composite material useful for assembling with bonding pieces made of materials having different thermal expansion coefficient.

The bonding constitutes an assembling technique, which found during these recent years more and more extensive application field due to its advantages. But classical solutions have disadvantages every time it is necessary to assemble two materials having very different expansion coefficients, such as glass and metal. In fact, temperature variations may, due to the assembly rigidity, cause the appearance of stresses such that the glue or the weaker material has to yield.

From the most currently used adhesives because they provide a particularly robust assembly, it is possible to mention the epoxy resin and especially the araldite. When people desire to assemble two materials having different expansion coefficients with araldite bonding, the following process is used. Both surfaces of a rubber film with suitable form is coated with resin added with a hardener, the so coated film is then placed between two pieces to be assembled and they are polymerized at about 100°C for 15 minutes in the case of araldite. Such process is ill adapted to mass production, especially in the automobile industry. In fact, use of liquid constituents necessitates numerous manipulations, time consuming and requires safety measures for protecting the workers in charge of the application. More especially when there is release of volatile products. Rubber film must be bonded apart, then placed between pieces when it is still sticky, this fact is often translated into inadvertent side motion during the placement in heating press for the polarization.

It was also proposed to use as adhesive a mixture of epoxy resin and nylon dispersed into the resin. If this solution provides satisfactory results with regard to the assembling reliability, even for large variations of temperature, on the other hand it has the disadvantage of requiring the application of adhesive in liquid phase or in the form of a film wherein two very

different components coexist. The film must be submitted with its entire thickness (important for supplying required suppleness) to polymerization.

The invention aims to provide a composite material useful for assembling pieces having different thermal expansion coefficients, the assembling which may later support very large temperature variations, responding better than prior bonding products to practical requirements, especially due to the fact of its easy-to-use and safety it offers.

For this purpose, the invention proposes a composite epoxy-elastomer, especially characterized by the fact that it comprises an elastomer film of at least 0.3 mm thick, coated on both surfaces with a solid film of thermosetting epoxy resin having a thickness ranging between 0.10 mm and 0.20 mm. The elastomer being of a type such that it is capable of resisting without loss of its properties to polymerization conditions of the resin, and advantageously, to the conditions of temperature wherein the resin is polymerized in a period less than ten minutes.

Practically, a fluorinated synthetic elastomer resistant to a temperature of at least 260°C will be advantageously used. This elastomer will be allowed to adopt higher polymerization temperature, and correlatively to perform this polymerization in few minutes.

The epoxy resin must be in the form of solid film on the ready-to-use composite. The epoxy resin must either have high molecular weight (at least 4,000), or be pre-polymerized during the composite production. In the first case, it is especially possible to use resins with atomic weight comprises between 4,000 and 5,000, polymerizing in few minutes at a temperature of 280°C or more when the resins are accompanied with a hardener while having long conservation period at low temperature and being soluble in volatile solvents.

The invention also aims to supply a manufacturing process of such composite in the form of very manageable roll. According to the invention, an elastomer strip or a sheet is successively circulated in a distributor that deposes a resin film which is dissolved or dispersed in volatile solvent, with heating means intended to evaporate the solvent and/or to pre-polymerize the resin to make one of the films. Then, in a position reverse with respect to the previous one, under new distributor and new heating means to make the other film.

The invention will be better understood at the reading of the following description of a composite making up a particular embodiment of the invention and its manufacturing process.

The description is made with reference to the unique figure, which accompanies it and shows an extremely schematic device for manufacturing the composite.

As it was said above, the composite according to the invention is made up with an elastomer film coated on both surfaces with a solid film of epoxy resin thermosetting at a temperature compatible with the elastomer performance. Elastomer film thickness must be at least 0.3 mm so that shearing stresses created by temperature variation under normal conditions of use do not attempt to tear this elastomer. Practically, a thickness 0.3 mm may be considered as a minimum. In fact, it also allows one to obtain reliable assembling when it is subjected to a temperature of about –40°C, this temperature is practically the minimum for elements designed to be exposed to outside atmosphere, such as automobiles, after the polymerization operation at a temperature of about 280°C, which allows rapid hardening of the resin. Maximum thickness is obviously function of the anticipated conditions of employ. But practically, it is advantageous to keep a value as low as possible, to reduce the bulkiness and, in most of the cases, a value of 0.5 mm will be close to the optimum.

The elastomer must obviously not to become brittle at the lowest temperatures to which it must be subjected to when in service.

Practically, a fluorinated synthetic elastomer will be advantageously used. The elastomer resists well to high temperatures. Among other elastomers of the same type, it is possible to mention, as particularly interesting, synthetic rubber made up with linear copolymer of vinylidene and hexafluoropropylene fluoride with molecular weight of about 60,000 and containing about 65% of fluorine, known under brand name "VITON". This elastomer resists at 200°C for 2,400 hours and may be temporarily brought to a temperature of 280°C, which is sufficient to the polymerization in few minutes of the most appropriate epoxy resins.

Each of the surfaces of the film is coated with an epoxy resin layer, which has at least 0.1 mm thick, whose continuity and regularity must be high.

Practically, a layer of 0.15 mm, which allows one to conciliate regularity and rapid polymerization, will provide in general a very satisfactory result.

From useful epoxy resins, it is possible to mention those that have molecular weight comprises between 4,000 and 5,000 (and therefore they are in solid form) mixed with a hardener made up with aldehyde condensation products, such as resins of urea, melanin and phenol-formaldehyde. Above-mentioned resins with high molecular weight remain soluble in solvent mixtures, such as mixtures of toluene or xylene with oxygenated materials and especially the ketones. Obtained solutions have low viscosity and may be spread without difficulty in the form of thin layer. Resin is preferably filled with nylon or the like. Resins in alcoholic solution are also useful.

Epoxy-rubber composite may be produced with the help of an installation of the type described in the attached unique figure. Rubber, in the form of strip with suitable width for the anticipated use, is stored on reel 1 mounted with free rotation. One should note that certain synthetic elastomers is ill adapted to the making of very long strip and in this case, the synthetic elastomers must be presented at the device entrance in the form of sheet. Strip 2 exiting from reel 1 is driven by two rollers 3 equipped with a driving mechanism (not shown here) and the strip passes under distributor 4 charged with a solution of epoxy-resin/hardener mixture. This distributor deposes on the upper surface of strip 2 a layer 5 with suitable thickness. The so coated strip then passes between one or several series of rollers, each series comprising a lower support roller 6 and an upper roller 7 for calibrating and regularizing. Then, the strip passes under heating means, schematized in the figure with infrared heating ramp 8. This part of the installation must obviously be ventilated; this fact does not pose any problem because of fixed station. On the other hand, solvents may partially recovered. Heating intensity and ramp length are chosen such that at the exit of these means the resin is in the form of a solid layer, therefore devoid of solvent. Moreover, in certain cases, it may be advantageous to pre-polymerize the resin, although this solution, which has the disadvantage of reducing later possible storage time,

is in general avoided when above solid resins provided as example is used.

Return rollers 9 and 10 reverse the circulation direction of strip 2 and make it circulate under new distributor 4', between one or several couples of rollers 6' and 7', and under heating ramp 8'. All these elements being very similar to those which are just described, it is not necessary to recall again their constitution.

Finally, the strip so coated on both surfaces is wound in a receiving reel 13 driven by means (not shown here), which maintains the strip under tension. Reel 12 provides in the same time an intercalate 11 designed to avoid that successive composite single turns adhere to each other. This intercalate may especially be a smooth polyvinyl chloride film.

The so obtained composite may be conserve before use for quite long periods, with the condition that it is maintained at low temperature, preferably below 0°C, to avoid spontaneous polymerization of the resin.

Use of composite results from previous description: piece with necessary form is cut from the strip, the piece is placed between two elements to be joined, one low contact pressure is in general sufficient to ensure adhesion, and the piece is heated at required temperature and duration to obtain complete hardening. Practically, it is in general enough to bring the resin film to a temperature of about 280°C for 2 minutes.

Composite according to the invention is susceptible of very diverse applications especially due to its easy-to-use. The resin does not release volatile products during its polymerization; this fact avoids the obligation of having safety measures. Allergy phenomenon encountered by workers who have to handle the resins in liquid phase are eliminated. Use speed is very high; this fact allows the application to mass production. It is possible, for example, to mention in the automobile industry, the fixing of windshield and rearview mirror, the assembling of body elements, one of which is metallic and the others made of eventually reinforced synthetic

materials, the fixing the elements for controlling window glasses to these body elements. In the aeronautical industry, it is also possible to fix coatings on honeycomb panels.

CLAIMS

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1. Epoxy-elastomer composite useful for assembling with bonding pieces of materials having different thermal expansion coefficients, characterized by the fact that it comprises a film of elastomer material with thickness at least equal to 0.3 mm coated on both surfaces with solid film of thermosetting epoxy resin having a thickness ranging between 0.10 mm and 0.15 mm, the elastomer being capable of resisting to temperature to which the resin is polymerized in a period less than 10 minutes.

2. Composite according to claim 1, characterized by the fact that the elastomer is a fluorinated synthetic elastomer resistant to a temperature of at least 260°C

3. Composite according to claim 2, characterized by the fact that the elastomer is a linear copolymer of vinylidene fluoride and hexafluoropropylene fluoride, having a molecular weight of about 60,000 and containing about 65% of fluorine.

4. Composite according to claims 1, 2 or 3, characterized by the fact that the resin is made up with intermediate epoxy itself and hardener.

5. Composite according to claim 4, characterized by the fact that the resin is filled with nylon.

6. Composite according to any one of previous claims, characterized by the fact that it is in the form of strip wound with a thin and smooth intercalate made of plastic material, such as polyvinyl chloride.

7. Manufacturing process of a composite according to claim 5, characterized by the fact that the strip is successively circulated under a distributor which deposes a resin film dissolved in volatile solvent, under heating means intended to evaporate solvent and/or pre-polymerize the resin, then in a reverse position with respect to the previous one, under a new distributor and new heating means.

8. Process according to claim 7, characterized by the fact that calibrating means placed between each distributor and heating means which follow it.

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